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### THE SYNTHESIS AND CHARACTERIZATION OF 10,11-BIS(HYDROXYIMINO)-4,8,12,17-TETRAAZA 1,2,19,20-O-DICYCLO-HEXYLIDENEOCTACOSENE AND SOME TRANSITION METAL COMPLEXES

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# THE SYNTHESIS AND CHARACTERIZATION OF 10,11-BIS(HYDROXYIMINO)-4,8,12,17- TETRAAZA 1,2,19,20-O-DICYCLO- HEXYLIDENEOCTACOSENE AND SOME TRANSITION METAL COMPLEXES

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In this study, a novel dioxime 10,11-bis(hydroxyimino)-4,8,12,17-tetraaza-1,2,19,20-O-dicyclohexylideneoctacosene (LH<sub>2</sub>) has been synthesized starting from 1,2-O-cyclohexylidene-4-aza-8-aminooctane, which has been prepared from the 1-chloro-2,3-O-cyclohexylidene, and dichloroglyoxime. The structure of this *vic*-dioxime has been determined as the (*E*, *Z*) form according to <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR data. Mononuclear complexes with a metal to ligand ratio of 1 : 2, except for UO<sub>2</sub>(VI), have been isolated with Co(III), Co(II), Cu(II) and Ni(II) salts. The metal to ligand ratio of the uranyl complex is 1 : 1 and it has a dimeric structure. Attempts to prepare trinuclear complexes of the ligand with Co(III), Co(II), Cu(II) and Ni(II), failed. The structure of the ligand and its complexes is proposed from elemental analyses, IR, UV–VIS, <sup>13</sup>C and <sup>1</sup>H NMR spectra, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

*Keywords:* Dioxime; transition metal complexes; uranyl

## INTRODUCTION

Macromolecules attached to dioximes and their transition metal complexes have been investigated.<sup>1,2</sup> *vic*-Dioximes have received considerable attention as model compounds which mimic biofunctions such as reduction of

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vitamin B<sub>12</sub>.<sup>3,4</sup> The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding.<sup>4</sup> The high stability of the complexes prepared with *vic*-dioxime ligands has been used extensively for various purposes. Compounds containing the 1,3-dioxolane group are used as solvents, additive compounds and corrosion retardants. Polymers containing the 1,3-dioxolane group exhibit semiconducting behavior. Polymers and copolymers of 1,3-dioxolane group also exhibit herbicidal and perfume activity.<sup>5,6</sup>

Gök has synthesized several ligands containing four aza or diaza-dithia groups and showed their capability of forming trinuclear complexes.<sup>7</sup> Gök *et al.* also have synthesized similar aza compounds attached to the dioxime group.<sup>8</sup> Similar compounds containing long alkyl chains were synthesized by Gürol *et al.*,<sup>9</sup> Ahsen *et al.*<sup>10</sup> and Gök.<sup>11</sup> Sevindir has synthesized hetero bis aza compounds and used them to complex with some transition elements.<sup>12</sup> In all the articles mentioned above, same complexation characteristics were observed since the ligands have mononuclear complexes that contain unsaturated sites.

The aim of the present study is to synthesize and characterize a new dioxime-containing diaza macrocycle and to obtain its mononuclear complexes with Co(III), Co(II), Cu(II), Ni(II) and UO<sub>2</sub>(VI). Herein we report the synthesis of a new dioxime ligand containing long alkyl chains.

## RESULTS AND DISCUSSION

The routes for synthesis of LH<sub>2</sub> (Figure 1) are given in Scheme 1. The first step is synthesis of 1-chloro-2,3-O-cyclohexylidene propane (1) from reaction

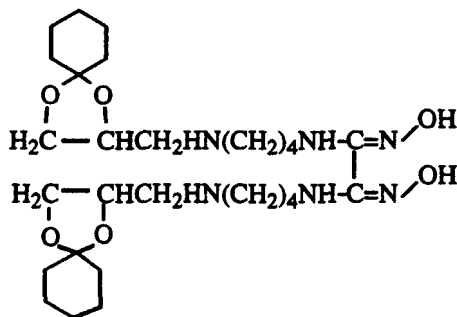
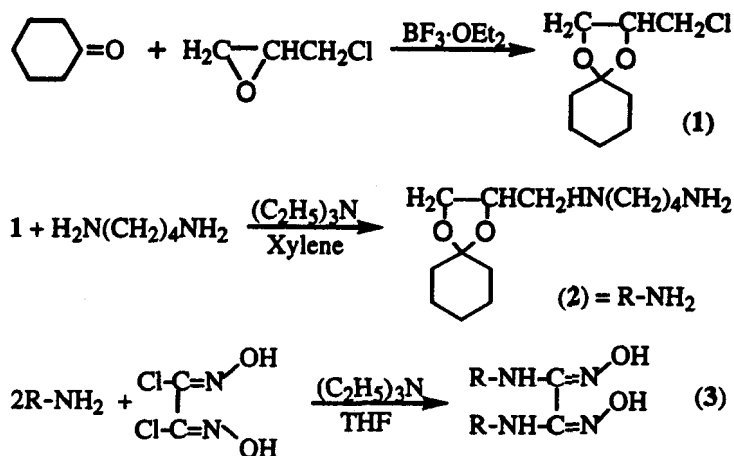


FIGURE 1 10,11-Bis(hydroxyimino)-4,8,12,17-tetraaza 1,2,19,20-O-dicyclohexylidene-octacosene, LH<sub>2</sub>.



SCHEME 1

of cyclohexanone and epichlorohydrin. In this reaction  $\text{BF}_3 \cdot \text{OEt}_2$  was used as a catalyst. In the second step, 1-chloro-2,3-O-cyclohexylidene-propane and 1,4-diaminobutane were reacted to obtain 1,2-O-cyclohexylidene-4-aza-8-aminooctane (2) (abbreviated as  $\text{R-NH}_2$ ). In the third step, 10,11-bis(hydroxyimino)-4,8,12,17-tetraaza-1,2,19,20-dicyclohexylideneoctacosene (3) was obtained from reaction of dichloroglyoxime, obtained from the procedure published previously,<sup>13</sup> and 1,2-O-cyclohexylidene-4-aza-8-aminooctane, Scheme 1.

Elemental analyses, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data confirmed the structures. Data are given in the experimental section and in Tables I–V.

In the IR spectrum of (1), the most characteristic peaks are at 1105 (oxolane) and  $745\text{ cm}^{-1}$  (C–Cl), and  $^1\text{H}$  NMR peaks are at 1.65, 3.24–3.57, 4.35 and 3.85–4.03 ppm. These belong to  $-\text{CH}_2-$  (in cyclo structure),  $-\text{O}-\text{CH}_2-$ ,  $-\text{O}-\text{CH}-$  and  $-\text{CH}_2-\text{Cl}$ , respectively.<sup>25</sup>

In the IR spectrum of (2), the characteristic peaks are at  $3336\text{--}3453\text{ cm}^{-1}$  which are assigned to  $\nu(\text{N-H})$  and  $\nu(\text{NH}_2)$  and the peak at  $1105\text{ cm}^{-1}$  is assigned to the  $\nu(\text{C-O})$  group. There is not a C–Cl stretch in the IR spectrum of (2). In the  $^1\text{H}$  NMR spectrum there are two characteristic resonances, at 1.30 and 3.56–3.80 ppm which belong to the N–H (identified by  $\text{D}_2\text{O}$  exchange) and  $-\text{O}-\text{CH}_2-$  groups, respectively. There is another  $-\text{O}-\text{CH}_2-$  peak at 3.46–3.39 ppm which is assigned to the other isomer of (2). Compound (2) has *cis-trans* isomers. 3.56–3.80 ppm is for the *cis* isomer and 3.46–3.39 ppm for the *trans* isomer.<sup>25</sup> The isomer ratio was found to be 55% *cis* and 45% *trans* isomer from the  $^1\text{H}$  NMR data. In the spectrum,

the  $-\text{CH}-\text{O}-$  peak is at 4.10, the  $-\text{CH}_2-$  (in cyclo structure) peak at 1.59 ppm, and the  $-\text{CH}_2-\text{CH}_2-$  (aliphatic) resonances are observed at 1.75 and 2.30 ppm as broad bands.

In the IR spectrum of  $\text{LH}_2$ , characteristic peaks appear at  $3412\text{ cm}^{-1}$   $\nu(\text{N}-\text{H})$ ,  $3259\text{ cm}^{-1}$   $\nu(\text{O}-\text{H})$ ,  $1637\text{ cm}^{-1}$   $\nu(\text{C}=\text{N})$ ,  $1105\text{ cm}^{-1}$   $\nu(\text{oxolane})$  and  $966\text{ cm}^{-1}$   $\nu(\text{N}-\text{O})$  as expected for a substituted *vic*-dioxime.<sup>15</sup> In the  $^1\text{H}$  NMR spectrum, since the OH protons of the oxime are not equivalent (*E, Z* form) two peaks were observed at 9.10 and 10.21 ppm and N-H protons at 5.09–5.63 ppm as singlets. Chemical shifts observed for N-OH and N-H disappeared upon addition of  $\text{D}_2\text{O}$  to the solution. Methylene  $-\text{CH}_2-\text{CH}_2-$  protons were observed at 2.54–2.62 ppm and 2.64–2.74 ppm as multiplets. There are two  $-\text{O}-\text{CH}_2-$  peaks, one at 3.45–3.94 and the other at 3.95–4.14 ppm, indicating that the ligand has *cis-trans* isomers in a ratio 58% *cis* and 42% *trans*.<sup>25</sup> In the  $^{13}\text{C}$  NMR spectrum, carbon resonances of dioxime groups were observed at 153.70 ( $\text{C}_{14}$ ) and 146.20 ( $\text{C}_{15}$ ) ppm; the  $\text{C}_6$  (ipso) carbon resonance is at 111.60 and 110.75 ppm.  $\text{C}_7$  and  $\text{C}_8$  carbons of the ligand have double resonances at (69.02 and 68.15) and (75.55 and 75.77) ppm, respectively. Observation of *vic*-dioxime and  $-\text{CH}_2-\text{CH}_2-$  protons in the  $^1\text{H}$  NMR, and of dioxime carbons in  $^{13}\text{C}$  NMR spectra at two different frequencies in each case, indicates that *vic*-dioxime has an *amphi* structure.<sup>16</sup> According to the elemental analyses, IR,  $^{13}\text{C}$  and  $^1\text{H}$  NMR results, the structure of ligand is consistent with that shown in Figure 2.

The ligand  $\text{LH}_2$ , on interaction with  $\text{Co(III)}$ ,  $\text{Co(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Ni(II)}$  and  $\text{UO}_2(\text{VI})$  salts, yields complexes corresponding to the general formula  $(\text{LH})_2\text{M}$ , or, in the case of  $\text{Co(II)}$ ,  $(\text{LH})_2\text{M} \cdot 2\text{H}_2\text{O}$ , and in the case of  $\text{UO}_2(\text{VI})$ ,  $(\text{LH})_2(\text{UO}_2)_2(\text{OH})_2$ . For  $\text{Co(III)}$  complexes having pyridine and imidazole, the complex formulas are  $(\text{LH})_2\text{Co}(\text{py})\text{Cl}$  and  $[(\text{LH})_2\text{Co}(\text{Im})\text{Cl}]\text{Cl}$ . The analytical data for all of these complexes are presented in Tables I–V.

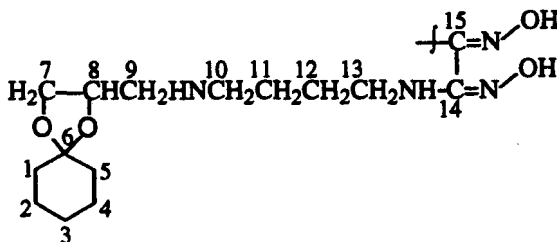


FIGURE 2 The structure of the ligand,  $\text{LH}_2$ .

TABLE I The colors, formulas, formula weights, melting points, yields and elemental analyses results of the ligand and the complexes

Compounds	Formula weights (g/mol)	Color	Melting point (°C)	Yield (%)	Elemental analyses % calculated (found)		
					C	H	N
R-NH <sub>2</sub> (2)					65.00	10.00	11.66
C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub>	242.21	Colorless		46	(65.20)	(9.89)	(11.80)
Ligand, LH <sub>2</sub>	568.77	Pale	99	80	59.13	9.22	4.78
C <sub>28</sub> H <sub>52</sub> N <sub>6</sub> O <sub>6</sub>		yellow			(58.85)	(9.12)	(14.40)
Co(LH) <sub>2</sub> · 2H <sub>2</sub> O	1234.51	Brown	210	68	54.49	8.98	13.62
C <sub>56</sub> H <sub>110</sub> N <sub>12</sub> O <sub>14</sub> Co					(54.10)	(9.11)	(13.98)
Co(LH) <sub>2</sub> (py)Cl	1313.03	Dark	216	63	58.80	8.52	13.87
C <sub>61</sub> H <sub>111</sub> N <sub>13</sub> O <sub>12</sub> ClCo		brown			(58.95)	(8.60)	(13.88)
[Co(LH) <sub>2</sub> (Im)Cl]Cl	1336.46	Dark	206	43	53.03	8.22	14.67
C <sub>59</sub> H <sub>109</sub> N <sub>14</sub> O <sub>12</sub> Cl <sub>2</sub> Co		green			(52.97)	(8.21)	(14.50)
Cu(LH) <sub>2</sub>	1203.10	Dark	124	69	55.91	8.88	13.97
C <sub>56</sub> H <sub>106</sub> N <sub>12</sub> O <sub>12</sub> Cu		green			(55.73)	(8.70)	(13.67)
Ni(LH) <sub>2</sub>	1198.26	Maroon	164	77	56.13	8.92	14.03
C <sub>56</sub> H <sub>106</sub> N <sub>12</sub> O <sub>12</sub> Ni					(56.06)	(8.60)	(13.92)
(UO <sub>2</sub> ) <sub>2</sub> (LH) <sub>2</sub> (OH) <sub>2</sub>	1713.59	Orange	238	55	39.25	6.33	8.91
C <sub>56</sub> H <sub>108</sub> N <sub>12</sub> O <sub>18</sub> U <sub>2</sub>					(39.50)	(6.36)	(8.61)

TABLE II Characteristic IR bands (cm<sup>-1</sup>) of the ligand and complexes as KBr pellets

Compounds	O-H	N-H	Aliph. C-H	O...H-O	N-O	C=N	Others
LH <sub>2</sub>	3259	3412	2953-2876	—	966	1637, 1625	—
(LH) <sub>2</sub> Ni	—	3361	2953-2876	1735	945	1603	—
(LH) <sub>2</sub> Co · 2H <sub>2</sub> O	3250-3580	3336	2953-2876	1730	943	1603	—
(LH) <sub>2</sub> Co(py)Cl	—	3438	2953-2876	1730	943	1614	1649 (C <sub>5</sub> H <sub>5</sub> N)
[(LH) <sub>2</sub> Co(Im)Cl]Cl	3259	3310	2953-2876	—	980	1626	1603 (C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> )
(LH) <sub>2</sub> Cu	—	3336	2953-2876	1740	944	1605	—
(LH) <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub>	3208-3512	3412	2953-2876	—	966	1637	920 (O-U=O)

TABLE III Characteristic UV-VIS bands of the ligand and complexes in DMF

Compounds	Wave length (nm)	μ <sub>eff</sub> (B.M.)
Ligand, LH <sub>2</sub>		286
Co(LH) <sub>2</sub> · 2H <sub>2</sub> O	417	290
Co(LH) <sub>2</sub> (py)Cl	435	336
[Co(LH) <sub>2</sub> (Im)Cl]Cl	415	330
Cu(LH) <sub>2</sub>		390
Ni(LH) <sub>2</sub>	432	332
(UO <sub>2</sub> ) <sub>2</sub> (LH) <sub>2</sub> (OH) <sub>2</sub>	435	354
		286
		2.32
		dia
		dia
		1.57
		dia
		dia

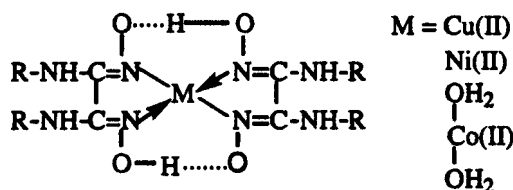
TABLE IV  $^1\text{H}$  NMR spectra of the ligand and some complex in  $\text{DMSO}-d_6$  in  $\delta$  (ppm)

Compounds	$N-H^a$	$N-CH_2$	$-CH_2-CH_2-^a$	Cyclo- $CH_2^*$	$>CH-O$	$-CH_2-O$	Others
$\text{LH}_2$	5.36 (4H) <sup>s</sup>	2.89-3.44 (12H) <sup>m</sup>	2.54-2.62 (4H) 2.64-2.74 (4H)	1.21-1.78 (20H)	4.15-4.19 (m, 1H) 4.22-4.35 (m, 1H)	3.95-4.14 (m, 2H) 3.45-3.94 (m, 2H)	9.10 (1H) <sup>s</sup> OH <sup>a</sup> 10.21 (1H) <sup>s</sup> OH <sup>a</sup>
$(\text{LH})_2\text{Co}(\text{py})\text{Cl}$	7.21 (8H) <sup>s</sup>	3.17-3.51 (24H) <sup>m</sup>	2.91-3.09 (16H)	1.18-1.90 (40H)	4.00-4.18 (m, 2H) 4.20-4.37 (m, 2H)	3.86-3.96 (m, 4H) 3.61-3.77 (m, 4H)	15.10 (2H) <sup>s</sup> (O-H...O) 7.58-8.81 (5H) ( $\text{C}_5\text{H}_5\text{N}$ ) <sup>*</sup> 6.73-7.91 (3H) ( $\text{C}_3\text{H}_3\text{N}_2$ ) <sup>*</sup> 8.92 (4H) <sup>s</sup> OH <sup>a</sup>
$(\text{LH})_2\text{Co}(\text{Im})\text{Cl}$	5.52 (8H) <sup>s</sup>	2.91-3.54 (24H) <sup>m</sup>	2.75-2.98 (16H)	1.00-1.82 (40H)	4.20 (m, 4H)	4.00 (m, 4H) 3.77 (m, 4H)	16.45 (2H) <sup>s</sup> (O-H...O)
$(\text{LH})_2\text{Ni}$	5.71 (8H) <sup>s</sup>	2.65-3.13 (24H) <sup>m</sup>	2.60-3.12 (16H)	1.10-1.83 (40H)	3.88-3.98 (m, 2H) 4.01-4.16 (m, 2H)	3.20-3.31 (m, 4H) 3.43-3.61 (m, 4H)	10.07 (1H) <sup>s</sup> OH <sup>a</sup> 11.35 (1H) <sup>s</sup> OH <sup>a</sup>
Uranyl comp. <sup>†</sup>	6.40 (8H) <sup>s</sup>	3.88-3.20 (24H) <sup>m</sup>	2.25-2.78 (16H)	1.18-1.57 (40H)	4.50 (m, 4H)	3.15-3.95 (m, 8H)	

<sup>a</sup>Deuterium exchangeable; <sup>m</sup>multiplet; <sup>s</sup>singlet. <sup>\*</sup>Broad bands; <sup>†</sup> $(\text{UO}_2)_2(\text{LH})_2(\text{OH})_2$ .

TABLE V TGA data of the ligand and complexes

Compounds	Stability	I. Step	II. Step	Weight loss %	Residue
Ligand, LH <sub>2</sub>	20-115	115-440	491-682	99	—
Co(LH) <sub>2</sub> · 2H <sub>2</sub> O	20-159	159-420	426-661	90	CoO
Co(LH) <sub>2</sub> (py)Cl	20-143	143-460	495-678	93	CoO
[Co(LH) <sub>2</sub> (Im)Cl]Cl	20-170	170-480	478-574	93	CoO
Cu(LH) <sub>2</sub>	20-134	134-490	503-704	93	CuO
Ni(LH) <sub>2</sub>	20-145	145-425	455-673	92	NiO
(UO <sub>2</sub> ) <sub>2</sub> (LH) <sub>2</sub> (OH) <sub>2</sub>	20-153	153-470	542-586	50	U <sub>3</sub> O <sub>8</sub>

FIGURE 3 Suggested structure of the square-planar and octahedral complexes of the ligand, LH<sub>2</sub>.

The metal to ligand ratio for Co(II), Cu(II) and Ni(II) complexes was found to be 1:2, but the Co(II) complex has two coordinated water molecules, in addition to the two ligand molecules. The infrared bands observed near 1637 and 1625 cm<sup>-1</sup> which are assigned to the  $\nu(\text{C}=\text{N})$  frequencies in the free ligand are shifted to lower frequencies after complexation. The shift of the C=N vibration to lower frequencies (1637-1603 cm<sup>-1</sup>) is due to N,N-metal coordination.<sup>15,19</sup> At the same time, the band observed at 966 cm<sup>-1</sup> in the free ligand which is assigned to the  $\nu(\text{N}-\text{O})$  is shifted to lower frequency after complexation, except for the [(LH)<sub>2</sub>Co(Im)Cl]Cl complex. On the other hand, a band not seen in the free ligand which is assigned to (O··H-O)<sup>17,18</sup> is observed at 1730 cm<sup>-1</sup> for Co(II), 1740 cm<sup>-1</sup> for Cu(II), 1735 cm<sup>-1</sup> for Ni(II) and 1730 cm<sup>-1</sup> for (LH)<sub>2</sub>Co(py)Cl. These absorptions indicate that the oxime group takes part in complexation.

In the <sup>1</sup>H NMR spectrum of the Ni(II) complex, there is no OH peak, as expected for the formula shown in Figure 3, but there is a band at 16.45 ppm which is assigned to (O··H-O).<sup>15,19</sup> The Cu(II) and Co(II) complexes are paramagnetic with magnetic susceptibility values of 1.57 and 2.32 B.M., respectively while the Ni(II) complex is diamagnetic. In the electronic spectra of these complexes there are intense M → L charge transfer bands, Table III. According to the above results a square-planar geometry for



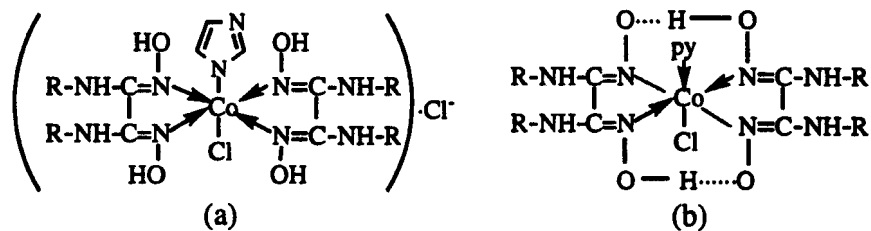


FIGURE 4 The suggested structure of the  $[(LH)_2Co(Im)Cl]Cl$  and  $(LH)_2Co(py)Cl$  complexes.

Ni(II) and Cu(II) complexes, and an octahedral geometry for Co(II) and Co(III) complexes are proposed.<sup>20–22</sup> Suggested structures of the complexes are shown in Figures 3 and 4.

In the IR spectrum of  $(LH)_2Co(py)Cl$ , characteristic peaks appear at 3438, 1730, 943, 1614 and  $1649\text{ cm}^{-1}$  which are assigned to  $\nu(N-H)$ ,  $\nu(O\cdots H-O)$ ,  $\nu(N-O)$ ,  $\nu(C=N)$  and pyridine ( $C_5H_5N$ ), respectively. Characteristic  $^1H$  NMR peaks are at 15.10 ppm for  $(O\cdots H-O)$  and 7.58–8.81 ppm for pyridine as expected for the complex formula shown in the Figure 4.

In the IR spectrum of  $[(LH)_2Co(Im)Cl]Cl$ , there are no  $(O\cdots H-O)$  peaks and oxime OH peaks still appear at  $3259\text{ cm}^{-1}$ ; the N–O stretches are different from those of free ligand. A peak at  $1603\text{ cm}^{-1}$  belongs to the imidazole ring. An  $^1H$  NMR spectrum of this complex shows a band at 6.73–7.91 ppm which belongs to the imidazole ring. A C=N–OH peak is observed at 8.92 and is  $D_2O$  exchangeable. These two Co(III) complexes are diamagnetic with intense  $M \rightarrow L$  charge transfers (Table III). Thus, both complexes are octahedral. Structures of the  $[(LH)_2Co(Im)Cl]Cl$  and  $(LH)_2Co(py)Cl$  complexes are shown in Figure 4.

The uranyl complex exhibits a different structure. In the IR spectrum, the  $UO_2(VI)$  complex shows a band at  $920\text{ cm}^{-1}$  which is assigned to  $\nu(O=U=O)$ <sup>22</sup> and there is not a  $O\cdots H-O$  band. The band observed at  $920\text{ cm}^{-1}$  is characteristic for  $O=U=O$  stretches and OH stretching vibrations of the oxime group still appear at  $3208\text{--}3515\text{ cm}^{-1}$  as a broad band. The  $^1H$  NMR spectrum of the uranyl complex shows two chemical shifts for the deuterium exchangeable N–OH at (10.07 and 11.35 ppm) and NH protons at (6.25 and 6.54 ppm). These spectral data indicate a binuclear  $\mu$ -hydroxo-bridged non-planar structure<sup>19</sup> for the uranyl complex of  $LH_2$ . This deep orange uranyl complex is diamagnetic and has a broad charge transfer band between 435–354 nm.<sup>23</sup> The suggested structure of the complex is shown in Figure 5.

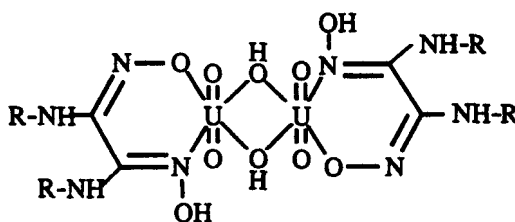


FIGURE 5 Suggested structure of the uranyl complex of the ligand, LH<sub>2</sub>.

## EXPERIMENTAL

1-chloro-2,3-O-cyclohexylidene propane (1), 1,2-O-cyclohexylidene-4-aza-8-amino octane (2) and 10,11-bis(hydroxyimino)-4,8,12,17-tetraaza 1,2,19,20-O-dicyclohexylideneoctacosene (3) were synthesized according to Scheme 1. Cyclohexanone and epichlorohydrine were purchased from Merck (Pure) and used without further purification. Dichloroglyoxime was synthesized by the method described in the literature.<sup>13</sup>

Elemental analyses were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey), IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using Hg[Co(SCN)<sub>2</sub>] as a calibrant; diamagnetic corrections were calculated from Pascal's constants.<sup>14</sup> The refractive index of the substances was determined on a Bellingam + Stanley Ltd. 60/70 Abbe (calibration oil RI = 1.47577 at 20°C) refractometer. Thermogravimetric (TGA) and differential thermal analyses (DTA) curves were recorded on a Shimadzu TG-50 thermobalance. Electronic spectra were recorded on a Sekomam S 1000 spectrometer.

### Synthesis of 1-chloro-2,3-O-cyclohexylidene Propane (1)

Fifteen to twenty drops of borontrifluoride etherate were added dropwise to 98 g (1000 mmol) cyclohexanone. Then 23 g (250 mmol) of epichlorohydrine was added dropwise to the reaction mixture at 10–17°C with continuous stirring. The reaction mixture was then further stirred for 2 h at 20°C. The product was distilled at 108–110°C and 13 mm Hg. Yield: 15.2 g (80%), relative density of the product was found to be 1.1484, using a pycnometer.

Refractive index of the product is  $n_D^{20} = 1.4772$ . Characteristic IR bands (NaCl cell,  $\text{cm}^{-1}$ ): 2953–2876 (C–H), 1105 (O–CH<sub>2</sub>–CH–O), 745 (C–Cl). Characteristic <sup>1</sup>H NMR bands (CCl<sub>4</sub>, TMS,  $\delta$  ppm): are at 1.65, 3.24–3.57, 4.35 and 3.85–4.03 ppm. These belong to –CH<sub>2</sub>– (in cyclo structure), –O–CH<sub>2</sub>–, –O–CH– and –CH<sub>2</sub>–Cl, respectively. Analysis (found %): C: 56.80; H: 7.75. Calculated (%) for C<sub>9</sub>H<sub>15</sub>ClO<sub>2</sub>: C: 56.69, H: 7.87.

### Synthesis of 1,2-O-Cyclohexylidene-4-aza-8-amino Octane (2)

13.3 g (151 mmol) of 1,4-diamino butane, 7.49 g (75 mmol) triethylamine and 50 mL absolute xylene were mixed in a reaction vessel and the temperature raised to 80°C. Then to this solution, a solution of 14.5 g (75 mmol) of (1) in 50 mL absolute xylene was added dropwise. The mixture was refluxed for 35 h with continuous stirring. After cooling to the room temperature the mixture was filtered and the filtrate distilled at 158–163°C and 5 mm Hg. Yield: 8.5 g (46%), relative density of the product was found to be 1.0430 using a pycnometer. Refractive index of the product is  $n_D^{20} = 1.4827$ . Characteristic IR bands (NaCl cell,  $\text{cm}^{-1}$ ): 3336–3453 (–NH, –NH<sub>2</sub>), 2953–2876 (C–H), 1105 (O–CH<sub>2</sub>–CH–O). Characteristic <sup>1</sup>H NMR bands (CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 1.75 and 2.30 (–CH<sub>2</sub>–CH<sub>2</sub>–, 4H, as broad band), 2.50–3.15 [N–CH<sub>2</sub>–, 6H, m], 3.56–3.80 and 3.46–3.39 [O–CH<sub>2</sub>–, 2H, m], 1.59 [cyclo–CH<sub>2</sub>–, 10H, as broad band], 4.10 [–CH–O, 1H, m], 1.30 [–NH, –NH<sub>2</sub>, 3H, s]. Characteristic <sup>13</sup>C NMR bands (CDCl<sub>3</sub>, TMS,  $\delta$  ppm, 90 MHz): 35.37 (C<sub>1</sub>), 23.81 (C<sub>2</sub>), 24.80 (C<sub>3</sub>), 24.10 (C<sub>4</sub>), 37.10 (C<sub>5</sub>), 110.13 (C<sub>6</sub>), 67.08 (C<sub>7</sub>), 75.10 (C<sub>8</sub>), 53.20 (C<sub>9</sub>), 50.00 (C<sub>10</sub>), 31.01 (C<sub>11</sub>), 25.39 (C<sub>12</sub>), 42.30 (C<sub>13</sub>).

### Synthesis of the Ligand (LH<sub>2</sub>)

A solution of 7.26 g (30 mmol) 1,2-O-cyclohexylidene-4-aza-8-amino-octane in 40 mL absolute THF was added to a solution of 3.03 g (30 mmol) triethylamine in 10 mL absolute THF. This mixture was cooled to –10 to –15°C and kept at this temperature, and a solution of 2.35 g (15 mmol) of dichloroglyoxime in 30 mL absolute THF was added dropwise under nitrogen with continuous stirring. Addition of dichloroglyoxime solution was carried out over a 1.5 h period. The mixture was further stirred 1 h and the temperature raised to 5°C. Precipitated triethylamine salt was filtered and the filtrate was evaporated to remove THF. The oily product was dissolved in 20 mL of CHCl<sub>3</sub> and precipitated with the addition of 100 mL of *n*-hexane. To obtain a high purity compound, crude product was dissolved in a limited amount

of methanol (5 mL) and precipitated by adding 100 mL of cold diethyl ether. Pure crystals were filtered and dried *in vacuo* at 30°C. Yield: 5.97 g (70%), m.p. 99°C (dec). Characteristic  $^{13}\text{C}$  NMR bands ( $\text{CDCl}_3$ , TMS,  $\delta$  ppm, 400 MHz): 37.60 ( $\text{C}_1$ ), 35.57 ( $\text{C}_2$ ), 27.39 ( $\text{C}_3$ ), 35.70 ( $\text{C}_4$ ), 37.25 ( $\text{C}_5$ ), 110.90 ( $\text{C}_6$ ), 69.02 and 68.15 ( $\text{C}_7$ ), 75.55 and 75.77 ( $\text{C}_8$ ), 53.07 ( $\text{C}_9$ ), 49.77 ( $\text{C}_{10}$ ), 24.24 ( $\text{C}_{11}$ ), 24.55 ( $\text{C}_{12}$ ), 55.23 ( $\text{C}_{13}$ ), 153.70 ( $\text{C}_{14}$ ) 146.20 ( $\text{C}_{15}$ ).

### Synthesis of the Complexes

A quantity of 0.400 g (0.70 mmol) of the ligand was dissolved in 10 mL absolute ethanol. A solution of 0.35 mmol of the metal salt [ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.084 g),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.061 g) and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.084 g)] in 5 mL ethanol was added dropwise with continuous stirring. The addition of Co(II) salt solution was carried out under nitrogen. The pH of the solutions decreased to about 3.0 and were adjusted to 5.0–5.5 by the addition of a 1% triethylamine solution in ethanol. Every mixture was further refluxed 2 h and the solutions were evaporated to about 5 mL. The complexes thus precipitated were kept on a water bath for 1 h at 50°C, then mixtures were cooled to room temperature and addition of 25 mL diethyl ether precipitated the complexes. Crystals of the complexes were filtered, washed with diethyl ether and cold ethanol and dried *in vacuo* at 60°C. A solution of 0.30 g (0.70 mmol)  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in 20 mL ethanol was added to a solution of 0.400 g of (0.70 mmol) ligand dissolved in 10 mL absolute ethanol. An orange colored complex was obtained which was stirred for 1 h at 40°C. The obtained compound was filtered, washed with diethyl ether and cold ethanol and dried *in vacuum* at 60°C.

In the synthesis of  $(\text{LH})_2\text{Co}(\text{py})\text{Cl}$ , a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.084 g, 0.35 mmol) in 20 mL THF was added to a solution of the ligand (0.40 g, 0.70 mmol) in 50 mL THF. Pyridine (0.069 g, 0.88 mmol) in 5 mL THF was added to the mixture and  $\text{O}_2$  was bubbled through the solution for 2 h while heating at 70°C. The mixture was evaporated to 5 mL. The complex was precipitated with the addition of 10 mL diethyl ether, filtered, washed with a limited amount of cold water and cold ethyl alcohol, and dried *in vacuo* at 60°C. In the synthesis of  $[(\text{LH})_2\text{Co}(\text{Im})\text{Cl}]\text{Cl}$ , the same procedure was used with imidazole substituted for pyridine (0.060 g, 0.88 mmol). Since this complex is soluble in water, water was not used to wash the product.

### Thermal Studies

The TGA curves in the temperature range 20–900°C show the copper and cobalt complexes to be thermally stable up to 134°C and 159°C,

TABLE VI DTA data of the ligand and complexes

Compounds	Exothermic peaks		Endothermic peaks		
Ligand, LH <sub>2</sub>	99, 713	224	320	561	659
Co(LH) <sub>2</sub> ·2H <sub>2</sub> O	397	210	493		
Co(LH) <sub>2</sub> (py)Cl	500	216	383	525	614
[Co(LH) <sub>2</sub> (Im)Cl]Cl	416	206	513	583	
Cu(LH) <sub>2</sub>	124	175	413	479	525
Ni(LH) <sub>2</sub>	389	164	231	462	560
(UO <sub>2</sub> ) <sub>2</sub> (LH) <sub>2</sub> (OH) <sub>2</sub>	417	238	282	394	435

respectively, whereas the nickel and uranyl complexes are thermally stable to 153°C and 145°C, respectively. (LH)<sub>2</sub>Co(py)Cl and [(LH)<sub>2</sub>Co(Im)Cl]Cl complexes are stable up to 143°C and 170°C respectively. The ligand, LH<sub>2</sub> is stable up to 115°C where its decomposition starts and finishes at 682°C. All the complexes decompose and produce the metal oxide in two steps in the temperature ranges 159–420°C and 426–661°C for Co(II), 134–490°C and 503–704°C for Cu(II), 145–425°C and 455–673°C for Ni(II), 153–470°C and 542–586°C for UO<sub>2</sub>(VI), 143–460°C and 495–678°C for (LH)<sub>2</sub>CoPyCl, 170–480°C and 478–574°C for [(LH)<sub>2</sub>Co(Im)Cl]Cl. The weight losses are approximately the same as the percentages estimated stoichiometrically from their chemical formulas given in Table I. All these complexes undergo complete decomposition to the corresponding metal oxides, CoO, CuO, NiO or U<sub>3</sub>O<sub>8</sub> (Table V). In the DTA curves of the ligand and complexes there are exo and endo peaks. All the complexes have only one exo peak while the ligand has two exo peaks, Table VI. The thermogravimetric (TGA) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10°C/min in a nitrogen atmosphere over a temperature range of 20–900°C.

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